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Rotational energy transfer in collisions between $\text{CO}(X^1\Sigma^+, v=2, J=0, 1, 4, \text{ and } 6)$ and He at temperatures from 294 to 15 K

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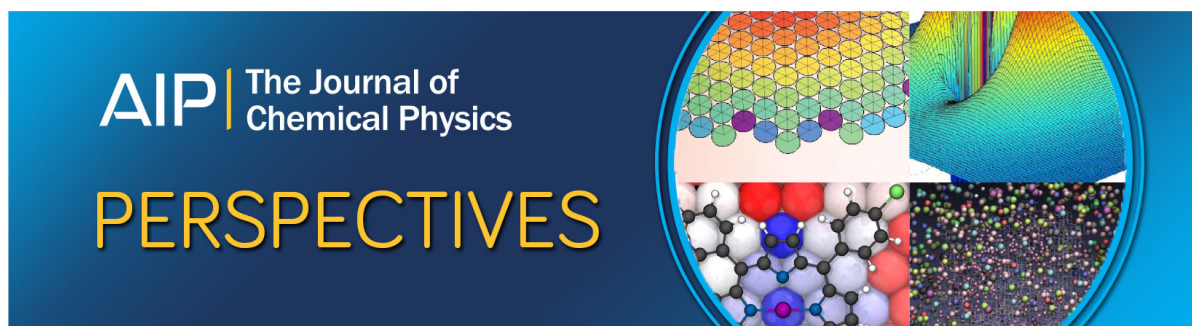
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Rotational energy transfer in collisions between CO($X^1\Sigma^+$, $v=2$, $J=0, 1, 4$, and 6) and He at temperatures from 294 to 15 K

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Infrared-vacuum ultraviolet double resonance experiments have been implemented in the ultracold environment provided by a Cinétique de Réaction en Ecoulement Supersonique Uniforme apparatus. With this technique rate coefficients of two kinds have been measured for rotational energy transfer in collisions between CO and He: (a) those for total removal from the selected rotational states $J=0, 1, 4$, and 6 in the vibronic state $X^1\Sigma^+$, $v=2$, and (b) those for transfer between selected initial and specific final states. Using different Laval nozzles, results have been obtained at several different temperatures: 294, 149, 63, 27, and 15 K. The thermally averaged cross sections for total removal by collisions with He show only slight variations both with initial rotational state and with temperature. The variation of state-to-state rate coefficients with ΔJ show several general features: (i) a decrease with increasing ΔJ ; (ii) a propensity to favor odd ΔJ over even ΔJ ; and (iii) at lower temperatures, the distribution of rate coefficients against ΔJ becomes narrower, and decreases in J are increasingly favored over increases in J , a preference which is most strongly seen for higher initial values of J . The results are shown to be in remarkably good agreement with those obtained in *ab initio* scattering calculations by Dalgarno and co-workers [Astrophys. J. **571**, 1015 (2002)]. © 2004 American Institute of Physics.
[DOI: 10.1063/1.1780163]

I. INTRODUCTION

The application of molecular beam and laser techniques has begun to provide very detailed information about collisions in which simple molecules are transferred between rotational levels in their electronic ground state. This increase in experimental information has been paralleled by progress in the theory of such processes, which has led, in turn, to an improved understanding of the factors that govern the nature and efficiency of inelastic collisions. A knowledge of the rates of rotational energy transfer are required to understand many gas-phase phenomena, including the propagation, absorption and dispersion of sound waves, the transport properties of gases, optical pumping processes, the pressure broadening of spectral lines, and the evolution of nonequilibrium population distributions formed, for example, in chemical reactions and supersonic expansions. The connections between these phenomena and inelastic collisions between CO and He are discussed briefly by Phipps *et al.*¹ and they cite 30 references to work in these connected fields.

Finally, and as a major stimulus for the work reported in this paper, a knowledge of the rates of rotational energy transfer in collisions at low temperatures is required to yield

a proper understanding of the relative intensities of rotational transitions observed, in emission, from dense interstellar clouds. Ever since the serendipitous discovery of millimeter-wave emission from CO in 1970,² the role of CO in molecular astrophysics cannot be overemphasized.³ In this regard, we note that CO is the second most prevalent molecule in the interstellar medium having an abundance of $\approx 10^{-4}$ relative to H_2 . Moreover, it is the most abundant dipolar molecule, so rotational transitions observed in emission from $^{12}C^{16}O$ and its isotopomers are frequently used to locate and map dense interstellar clouds⁴ both in the Milky Way⁵ and in other galaxies.⁶ In addition, because of its abundance, emission from rotational states of CO with $J>0$ provides an important cooling mechanism in the interstellar medium.⁷ Finally, in this brief survey, we note that comparisons of the intensities of emission from different rotational levels and different isotopomers of CO enable the physical conditions in different regions of the interstellar medium to be estimated.⁸ However, it is necessary for such calculations, as well as for estimates of the radiative cooling rate, to know the rate coefficients for transfer between different rotational levels of CO in collisions with the major interstellar species, H_2 , H, and He.

In many ways, collisions between CO molecules in their ($X^1\Sigma^+$) electronic ground state and He atoms provide an ideal test case for comparisons between experiment and theory, not least because it is one of the few heavy rotor-noble gas atom systems for which it should be possible to calculate the potential energy surface that governs the collision dynamics very accurately. The accuracy of both these *ab initio* calculations and of the scattering calculations per-

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formed on the selected potential energy surface has been tested by a wide variety of experiments. Thus De Lucia and co-workers^{9,10} have published the results of a number of studies of pressure broadening and line shifts for rotational lines in CO in a background of helium. Using a "collisional cooling" technique, these experiments have been performed at temperatures as low as 1.19 K,¹⁰ which is important, since only at such low temperatures do the results become sensitive to the small van der Waals well on the CO-He potential. This feature of the intermolecular potential has also been explored, even more directly, in spectroscopic experiments on the CO-He complex formed at low temperatures.¹¹

Compared, for example, with NO,^{12,13} there have been relatively few experiments that have directly examined rotational energy transfer in collisions between CO and He, and very few indeed that have obtained data at the state-to-state level; that is, which have provided rate coefficients or cross sections for transfer between defined initial and final states. In a series of papers,¹⁴ Belikov, Smith and their co-workers have sought to derive such rate constants by observing the evolution of CO rotational level populations in the environment of a free jet expansion, in which the main gas is He. However, such methods are not state resolved. Consequently, the interpretation of their observations is complex and relies on the details of the state-to-state rate coefficient matrix that is assumed.

More recently, two papers have reported results that can be more directly compared with the data that we report in the present paper. Antonova *et al.*,¹⁵ using a crossed beam apparatus and detecting CO state-specifically with a 2+1 resonantly enhanced multiphoton ionization scheme, have derived *relative* integral cross sections for rotational excitation of CO from its two lowest rotational levels, $X^1\Sigma^+$, $v=0$, $J=0$ and 1, in collisions with He at collision energies of 72 and 89 meV (6.95 and 8.6 kJ mol⁻¹). For small changes in J , the observed cross sections display oscillatory structure, as predicted by theory,^{16,17} with odd changes in J being favored over even changes, but this structure decreases for higher ΔJ and the cross sections decrease smoothly. The results were compared with those of scattering calculations and it was agreed that the *ab initio* surface obtained by Heijman *et al.*¹⁸ using symmetry adapted perturbation theory (SAPT) gives a satisfactory description of the repulsive wall of the CO-He potential energy surface, although it should be noted that the results of Antonova *et al.* would be insensitive to the attractive part of the potential, since their collision energies are much greater than the van der Waals well depth. Heijman *et al.* found a minimum on the CO-He potential of -23.734 cm⁻¹ (0.284 kJ mol⁻¹), with the ground state of CO-He possessing a dissociation energy of only 6.79 cm⁻¹ (0.081 kJ mol⁻¹).

Because CO state selection was achieved in a supersonic expansion, the measurements of Antonova *et al.*¹⁵ were confined to relative cross sections for transitions from $J=0$ and 1, the levels which contained the bulk of the rotational distribution after the expansion. On the other hand, double resonance (DR) methods offer the possibility of obtaining data from a wider set of initial levels and can also yield *absolute* values for the derived rate coefficients. Phipps *et al.*¹ have

employed an infrared-infrared (IR-IR) version of the DR method to investigate state-to-state rotational energy transfer in CO-CO collisions at room temperature. They employed a pulsed optical parametric oscillator to promote CO molecules to a selected rotational level (J_i) in $v=2$ and then monitored the evolution of population in this and other $v=2$, J levels by observing absorption on lines in the (3,2) vibrational band using a tunable cw diode laser. The data were analyzed by numerically solving the master equation and yielded rate coefficients for *total removal* and for *state-to-state transfer* from 29 initial levels. In contrast to the results of Antonova *et al.*¹⁵ for CO-He collisions, Phipps *et al.*¹ reported that, for CO-CO collisions, even ΔJ processes were favored for transitions with low J values.

Very recently, Smith *et al.*¹⁹ have published experimental data on CO-He rotational energy transfer using the same IR-IR DR technique at room temperature. CO was excited into specific rotational levels (J_i) in $v=2$ ranging from $J_i=2-9$ and populations monitored in $J_f=1-10$ as described above. These data were fitted using a Master equation approach, coupled either with one of a number of scaling laws, or with state-to-state rate coefficients which they calculated using the potential surface of Heijmen *et al.*¹⁸ They found that their data could be fitted extremely well using these calculated rate coefficients, and saw in this agreement strong evidence for the accuracy of the Heijmen *et al.* surface.

The present paper reports DR experiments on rotational energy transfer in CO-He collisions at temperatures down to 15 K. Like Phipps *et al.*,¹ we have used a pulsed IR laser source to promote CO molecules to selected rotational levels J_i in CO($X^1\Sigma^+$, $v=2$). However, in contrast to them, we have employed vacuum ultraviolet (VUV) laser-induced fluorescence (LIF) to observe molecules in specific rotational levels in CO($X^1\Sigma^+$, $v=2$). This technique has been implemented, using several different Laval nozzles, in the low temperature environment that can be provided in a CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus,¹³ and we report data for several temperatures: 294, 149, 63, 27, and 15 K. Measurements at such low temperatures are advantageous because the results of the collisions should be particularly sensitive to the attractive part of the potential energy surface and, in addition, not only is the average collision energy reduced as the temperature is lowered, but also the spread of collision energies is narrowed. On the other hand, as the temperature is lowered, the range of J levels that can be accessed is reduced, as a result of the narrowing of the rotational state distribution in the $v=0$ level from which molecules are promoted by an allowed ($\Delta J = \pm 1$) infrared transition.

The general technique that we employ here has now been rather widely used, not least in our own laboratory, to obtain rate coefficients for rotational energy transfer in simple molecules. In particular, James *et al.*¹³ have reported experiments like our own on rotational energy transfer in NO($X^2\Pi_{1/2}$, $v=3$) in collisions with He, Ar, and N₂ at temperatures down to 7 K. However, performing such measurements on CO introduces an extra level of experimental difficulty. In NO, the probe laser can be operated in the ultraviolet (UV) region of the spectrum at wavelengths

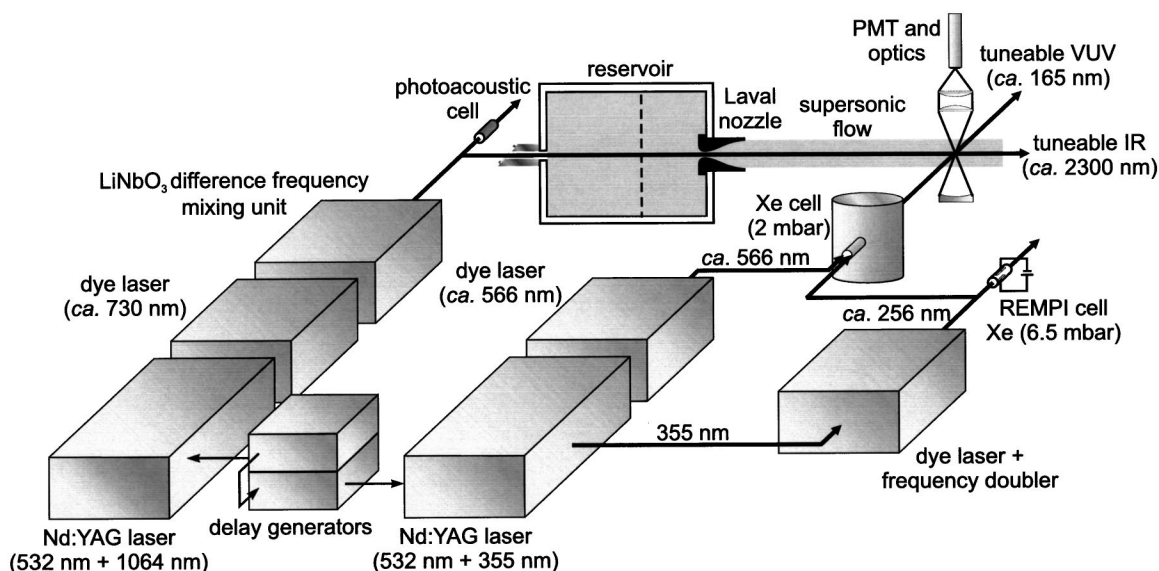


FIG. 1. A schematic diagram of the CRESU apparatus adapted for the study of rotational energy transfer in collisions between $\text{CO}(X^1\Sigma^+, v=2, J)$ and He using the IR-VUV DR technique.

which can be accessed quite straightforwardly by frequency doubling the output of a commercially available, pulsed dye laser. However, the $A^1\Pi-X^1\Sigma^+$ electronic transition in CO lies to much shorter wavelengths than the lowest electronic transition in NO and its excitation therefore requires the creation of pulses of tunable laser radiation in the VUV part of the spectrum. This requirement may explain why there have been no previous reports of the kinds of DR experiment that we describe here, even at room temperature.

Two kinds of IR-VUV DR (or IR-UV DR) experiment can be performed. In the first kind, which we refer to as a *kinetic* experiment, we follow the evolution of population in a single rotational level, usually J_i ; that is, the level directly populated by absorption of radiation from the IR pump laser. The frequency of the “probe” laser is fixed to that of an absorption line from the selected level and the intensity of the LIF signal is measured as the time delay between the pulses from the IR pump and the VUV (or UV) probe lasers is systematically varied. If the probe laser is set to monitor population in J_i , then such experiments yield the rate coefficient for total removal from J_i . In the second kind of experiment, which we refer to as a *spectroscopic* experiment, the time delay between the two laser pulses is set to correspond to a fraction of the average time between collisions in the gas sample, and the frequency of the probe laser is scanned to record a DR spectrum. The intensities of lines in this spectrum reflect the populations created by collisions in levels other than J_i at the instant that the probe laser is fired, and they yield values of the state-to-state rate coefficients for transfer between J_i and other rotational states J_f . We report the results of both kinds of experiment in the present paper.

II. EXPERIMENT

The apparatus and general technique employed in the present experiments are very like those used in the IR-UV DR experiments of James *et al.*¹³ on rotational energy transfer in collisions between $\text{NO}(X^2\Pi_{1/2}, v=3, J)$ and He, Ar,

and N_2 . A schematic of the apparatus is given in Fig. 1. The Birmingham CRESU apparatus was used both in the measurements of James *et al.* and in our own experiments, and their paper contains a full description of the characteristics and capabilities of this apparatus. The methodology of the present work differs from that of James *et al.* mainly in the techniques that have been employed: (i) to excite the target molecule, here CO, to selected rotational levels in a particular vibrational state of the electronic ground state, $\text{CO}(X^1\Sigma^+, v=2)$, and (ii) to observe CO molecules in specific levels ($X^1\Sigma^+, v=2, J$) and how these populations evolved in time following excitation to a selected initial level (J_i).

A. The CRESU apparatus

The CRESU technique²⁰ provides a means of preparing a uniform and fairly dense gas sample (10^{16} – 10^{17} molecule cm^{-3}) at a defined low temperature, while avoiding the problems of condensation associated with cryogenic cooling. The heart of a CRESU apparatus is a convergent-divergent Laval nozzle. Isentropic expansion of a preprepared gas mixture through this nozzle produces a jet of gas in which the temperature, density, and velocity are constant and which retains its uniformity for several tens of centimeters. A different nozzle, each with a unique nozzle profile, is required to obtain a particular temperature and density for a given carrier gas, here helium. The temperatures and densities attained in the present experiments are listed later in Table I. In the present experiments, the gas samples consisted of <1% of CO in helium and the effects of CO-CO collisions could be ignored.

All further details of the CRESU apparatus employed in the present experiments can be obtained by reference to the paper by James *et al.*¹³

TABLE I. Rate coefficients ($k/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and thermally averaged cross sections ($\langle\sigma\rangle/\text{\AA}^2$) for the removal of CO from selected rotational levels J_i in $X^1\Sigma^+$, $v=2$ in collisions with He at 15, 27, 63, 149, and 294 K.

T/K	$[\text{He}]/10^{16} \text{ molecule cm}^{-3}$	J_i	$k_{1st,J_i}/\mu\text{s}^{-1}$	$1-f_{J,e}$	$k_{1st,J_i,f}/\mu\text{s}^{-1}$	$k_{J_i,\text{all } f}/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\langle\sigma\rangle/\text{\AA}^2$
15	5.05	0	4.79 ± 0.40	0.829	4.12 ± 0.33	8.2 ± 0.6	27.2 ± 2.1
		1	6.55 ± 0.98	0.643	4.21 ± 0.63	8.34 ± 1.2	27.8 ± 4.1
		4	5.61 ± 0.36	0.960	5.39 ± 0.35	10.7 ± 0.7	35.5 ± 2.3
		6	5.93 ± 0.35	0.999	5.92 ± 0.35	11.7 ± 0.7	39.1 ± 2.3
27	4.65	0	5.78 ± 0.52	0.903	5.22 ± 0.47	11.1 ± 1.0	27.3 ± 2.5
		1	6.05 ± 0.66	0.761	4.60 ± 0.50	9.8 ± 1.1	24.2 ± 2.6
		4	6.41 ± 0.56	0.883	5.66 ± 0.49	12.0 ± 1.0	29.7 ± 2.6
		6	5.46 ± 0.36	0.982	5.36 ± 0.35	11.9 ± 0.8	29.4 ± 2.0
63	2.06	0	3.95 ± 0.22	0.958	3.78 ± 0.21	18.4 ± 1.1	29.8 ± 1.7
		1	3.50 ± 0.40	0.883	3.09 ± 0.35	15.1 ± 1.7	24.5 ± 2.7
		4	4.25 ± 0.58	0.839	3.57 ± 0.49	17.5 ± 2.4	28.3 ± 3.9
		6	3.67 ± 0.42	0.910	3.34 ± 0.38	16.2 ± 1.9	26.2 ± 3.0
149	1.44	1	3.87 ± 0.16	0.948	3.67 ± 0.15	25.5 ± 1.0	26.9 ± 1.1
		4	4.14 ± 0.26	0.887	3.67 ± 0.23	25.5 ± 1.6	26.88 ± 1.7
		6	4.29 ± 0.22	0.890	3.82 ± 0.20	26.5 ± 1.3	27.95 ± 1.4
294	5.35	1	16.63 ± 0.40	0.973	15.89 ± 0.39	29.7 ± 0.7	22.3 ± 0.6
	5.35	4	17.97 ± 0.54	0.931	16.73 ± 0.50	31.3 ± 0.9	23.5 ± 0.7
	5.34	6	20.73 ± 2.74	0.919	19.05 ± 2.52	35.7 ± 4.7	26.8 ± 3.5

B. The IR-VUV DR technique

In the present experiments, pulses of tunable IR radiation were generated using a frequency-mixing technique. The pulsed output (ca. 1110 mJ per pulse) from an injection-seeded Nd:yttrium aluminum garnet (YAG) laser (Continuum, Precision II) was frequency doubled in a β -BaB₂O₄ (BBO) crystal to yield pulses of ca. 500–550 mJ at 532 nm. This radiation pumped a dye laser (Sirah, Cobra Stretch) which, when operated on Pyridine 2 dye in methanol, generated pulses of 80–90 mJ energy and which could be tuned between 725 and 738 nm. The dye laser beam was aligned through a double Fresnel rhomb and combined with 100–120 mJ of the residual fundamental output from the Nd:YAG laser on a dichroic mirror. These two copropagating laser beams then passed through a LiNbO₃ crystal, which was held at 80 °C, to generate by difference frequency mixing pulses of infrared radiation that contained 5–10 mJ energy per pulse. This output, which had a line width of ca. 0.06 cm⁻¹, could be tuned between 2.274 and 2.408 μm , a range that covered an appreciable portion of the (2,0) vibrational overtone band of CO. In practice, P-branch transitions in this overtone band were used to promote CO molecules to selected rotational states in the ($X^1\Sigma^+$, $v=2$) state.

The present experiments on rotational energy transfer in CO and those of James *et al.*¹³ on rotational energy transfer in NO differ mainly in respect of the state-specific observation of the molecules excited by the IR pump laser. In the case of NO, molecules were promoted to selected rotational levels in the $X^2\Pi_{1/2}$, $v=3$ state and these molecules were then observed by exciting LIF at ca. 258–259 nm in the (0,3) band of the ($A^2\Sigma^+-X^2\Pi$) system. In the case of CO, the lowest electronic transition lies to much shorter wavelength, and consequently it was necessary to generate VUV laser radiation in order to observe CO in specific rotational levels

of the ($X^1\Sigma^+$, $v=2$) state. In practice, earlier experiments in our group on reactions of C atoms in their 3P_J electronic ground state²¹ had made use of VUV LIF to observe kinetic decays of the C atoms, and the method used there to generate pulses of VUV laser radiation was adapted for use in the present experiments.

In the present experiments, CO in specific rotational levels of the ($X^1\Sigma^+$, $v=2$) state was observed by exciting LIF in the (0,2) band of the ($A^1\Pi-X^1\Sigma^+$) system, which has its origin at 165.325 nm. The spectrum consists of P , Q , and R branches, though it should be noted for this type of system $P(1)$ and $Q(0)$ transitions are absent, and consequently CO($J=0$) is only detectable via the $R(0)$ transition. Unfortunately, the R branch possesses a band head [in the region of the $R(4)$ – $R(6)$ transitions], and is thus susceptible to overlap at higher temperatures.

Pulses of VUV laser radiation were generated using two photon resonant four-wave mixing in xenon gas²² and the implementation of this method in the CRESU apparatus is described in some detail elsewhere.²¹ Briefly, dye laser radiation was tuned to 255.94 nm in order to excite Xe in a two-photon transition to the $5p^56p[2^{1/2},2]$ state. Radiation from a second pulsed dye laser, aligned with the beam from the first and fired simultaneously could be tuned through the wavelength range from 565 to 567.5 nm to generate VUV radiation between 165.29 and 165.50 nm. This radiation propagated horizontally and, as shown in Fig. 1, was directed perpendicular to the gas flow in the CRESU chamber.

For kinetic measurements, the frequency of the VUV probe laser was set to that of an absorption from the J_i level in CO($X^1\Sigma^+$, $v=2$), where J_i denotes the rotational level to which CO molecules were directly excited by absorption of radiation from the IR pump laser. Using a solar blind photomultiplier tube (Thorn EMI 9403B) mounted behind an in-

terference filter, centered at 158.9 nm with a bandwidth of 23.4 nm (Acton Research), and above the gas flow, LIF signals were recorded as the time delay between the pulses from the IR pump and VUV probe lasers was systematically varied. In *spectroscopic* measurements, the time delay between the pulses from the IR pump and VUV probe lasers was fixed at a small value (30 ns, except for the experiments at 294 K, where it was 15 ns), and the frequency of the visible dye laser, and hence that of the VUV radiation, was scanned to record the relative LIF intensities of a number of lines in the ($X^1\Pi, v=0-X^1\Sigma^+, v=2$) band.

The tunability of the IR pump laser meant that, in principle, two kinds of spectroscopic experiments could be performed. In all of the experiments whose results are reported here, the frequency of the IR “pump” source was fixed and the frequency of the VUV probe laser source was scanned, as described in the previous paragraph. The results that these experiments yielded were judged to be superior to those from the smaller number of experiments that were performed with the frequency of the VUV laser fixed and that of the IR laser scanned.²³ The frequency of the IR pump laser could be tuned into resonance with the required transition in the first overtone band of CO by recording part of this band by photoacoustic methods using a small spectrophone cell containing 20 Torr of CO.

III. ANALYSIS OF EXPERIMENTAL RESULTS

In this section we describe briefly how we analyzed our experimental observations so as to yield both (a) rate coefficients for total removal of CO from selected rotational levels in the $X^1\Sigma^+, v=2$ state, and (b) rate coefficients for transfer in single collisions between these selected initial levels (J_i) and specific final levels (J_f). The methods used are essentially those described by James *et al.*¹³

A. Rate coefficients for total removal from selected rovibronic levels

In all the kinetic experiments, in which LIF signals were observed at different time delays (t) from the initially selected level J_i , the variation in the intensity of these signals (I_{LIF}) with t could be fitted to a single exponential. However, the signals did not decay to zero (i.e., to the value recorded before the IR pump laser was fired) but rather to a signal appropriate to the thermally equilibrated population in $X^1\Sigma^+, v=2, J_i$. Two examples of this behavior are illustrated in Fig. 2. In panel (a), which records the variation of I_{LIF} with t from CO($X^1\Sigma^+, v=2, J_i=6$) at 15 K, the signal does indeed decay to its baseline value, since the fractional rotational population in $J=6$ at 15 K is only 0.0012. In panel (b), however, which records the variation of I_{LIF} with t from CO($X^1\Sigma^+, v=2, J_i=1$) at 15 K, the signal decays at longer times to a value which is a significant fraction of its value immediately after firing the IR pump laser, reflecting the fact that the fractional rotational population in $J=1$ at 15 K is 0.36. We note here that vibrational relaxation by He or self-relaxation by the small fraction of CO included in the gas mixture was very slow on the time scale of these experiments.²⁴ The only other loss mechanism for CO($X^1\Sigma^+, v=2, J_i$) in this experiment is by diffusion out of

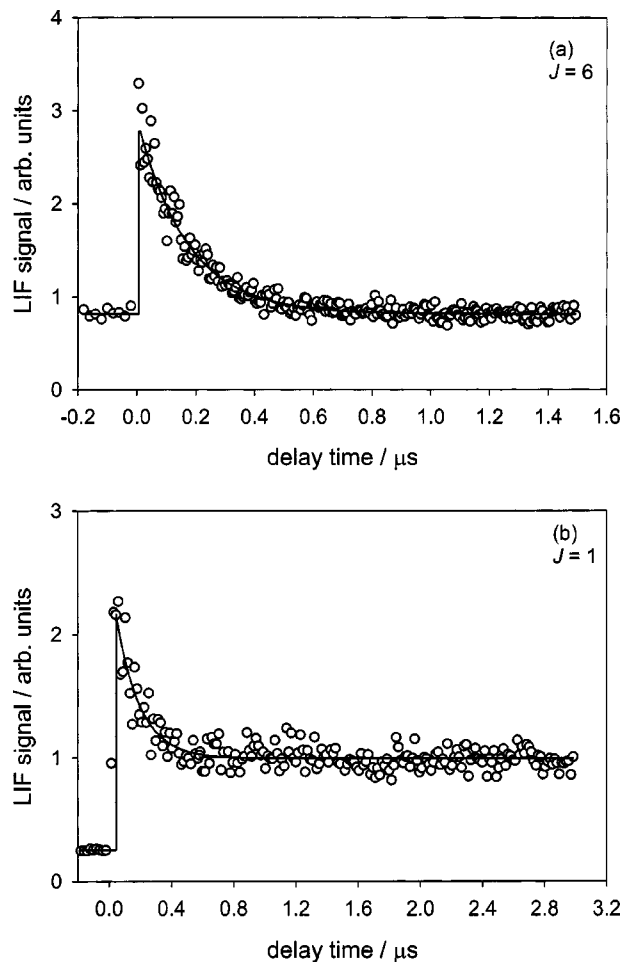


FIG. 2. Examples of the decays of LIF signals (open circles) in kinetic experiments at $T=15$ K where the probe laser is used to follow the decay in populations in the initially pumped level J_i as the delay between the pulses from the IR pump and VUV probe lasers is varied, fitted to single exponential decays (solid lines): (a) shows the result of an experiment on CO($X^1\Sigma^+, v=2, J_i=6$), and (b) shows the result of an experiment on CO($X^1\Sigma^+, v=2, J_i=1$).

the detection zone, which under the current experimental conditions is negligibly slow on the time scale of rotational relaxation.

Because the population in J_i does not generally relax to zero, the first-order rate coefficient (k_{1st, J_i}), found by fitting the LIF signals to a single exponential decay, as shown in both panels of Fig. 2, is related to the rates of transfer both out of and into the level J_i and the rate equation for this population (N_{J_i}) is²⁵

$$dN_{J_i}/dt = - \sum_j k_{J_i, j} N_{J_i} [\text{He}] + \sum_j k_{j, J_i} N_j [\text{He}] \quad (1a)$$

$$= -k_{J_i, \text{all}} N_{J_i} [\text{He}] + \sum_j k_{j, J_i} N_j [\text{He}], \quad (1b)$$

where N_{J_i} and N_j are the concentrations of CO in the initial (J_i) and in other ($J \neq J_i$) individual rotational levels, $[\text{He}]$ is the concentration of helium in the gas flow, and $k_{J_i, j}$ and k_{j, J_i} are the rate coefficients for transfer from J_i to j and from j to J_i , respectively.

To obtain the first-order rate coefficient for total transfer out of the level (i.e., $k_{1st,J_i,f} = k_{J_i,all J}[\text{He}]$) from k_{1st,J_i} , we assume that the second term on the right of Eq. (1b) can be written as $\sum_J k_{J,J_i}[\text{He}]\sum_J N_J$, so that Eq. (1b) becomes

$$\begin{aligned} dN_{J_i}/dt &= -k_{J_i,all J}[\text{He}]N_{J_i} + k_{all J,J_i}[\text{He}]N_{all J} \\ &= -(k_{J_i,all J} + k_{all J,J_i})[\text{He}]N_{J_i} + k_{all J,J_i}[\text{He}]N_{J_i}^0, \end{aligned} \quad (2)$$

where $N_{J_i}^0$ is the concentration of molecules initially promoted to J_i (and hence the *total* concentration in all J levels of $v=2$ on the time scale of these experiments), and $(k_{J_i,all J}/k_{all J,J_i})$ is the ratio of populations in J_i and in all other rotational levels at thermal equilibrium (i.e., when $dN_{J_i}/dt=0$).

Equation (2) corresponds to the equation often encountered in “relaxation kinetics”,²⁶ whereby a two-state system relaxes exponentially to equilibrium with a first-order rate coefficient given by the sum of the forward and reverse rate coefficients. In passing from Eq. (1b) to Eq. (2) we have assumed that the system can be treated as a two-level system comprising the initially excited rotational state and a set of Boltzmann-like distributions over the destination states that can be described by the same temperature as the final distribution. In this case, the fractional contribution to total back transfer from different levels is the same at all times. Of course, the correction for back transfer implied by this is only significant for the rather small number of cases where the fraction of molecules at thermal equilibrium in the initially excited level is large, that is, for the most populated rotational states at very low temperatures.

The solution of Eq. (2) predicts that the population N_{J_i} decays exponentially to the equilibrium population in J_i with a first-order rate constant given by

$$k_{1st,J_i} = (k_{J_i,all J} + k_{all J,J_i})[\text{He}]. \quad (3)$$

The ratio $(k_{J_i,all J}/k_{all J,J_i})$ is the ratio of the populations $(N_{J_i}/N_{all J})$ at equilibrium. Consequently, it is straightforward to show that

$$k_{1st,J_i} = k_{J_i,all J}[\text{He}] = k_{1st,J_i}(1 - f_{J_i,e}), \quad (4)$$

where $f_{J_i,e}$ is the fraction of molecules in level J_i when equilibrium is established amongst the rotational levels, and can be easily calculated via statistical mechanics.

The second-order rate constants for relaxation from selected rotational levels, i.e., $k_{J_i,all J}$, were calculated by dividing k_{1st,J_i} by $[\text{He}]$, the density of the helium carrier gas in the flow. The fact that the CO was present as less than 1% of the gas mixture justifies its neglect in this final part of the calculation.

B. Rate coefficients for state-to-state rotational energy transfer

To determine state-to-state rate coefficients, we adopted the same method as in earlier low temperature experiments from our laboratory on rotationally inelastic collisions of

$\text{NO}(X^2\Pi_{1/2}, v=3, J)$.^{12,13} This method requires the recording of two LIF DR spectra recorded at different fixed delay times. The first spectrum is recorded at a delay (δt) that is short compared with the relaxation time from the selected level in collisions between CO molecules and He atoms, so that one can neglect the transfer of molecules in secondary collisions and attribute the observed populations entirely to the result of collisions between CO molecules in the level J_i and He atoms. Under these conditions, the rate of population transfer into any collisionally populated level J_f can be described by the equation

$$dN_{J_f}/dt = k_{J_i,J_f}N_{J_i}[\text{He}], \quad (5)$$

which, if δt is sufficiently short, can be recast in the approximate form

$$k_{J_i,J_f} = (\delta N_{J_f}/N_{J_i}^0)/\delta t[\text{He}], \quad (6)$$

where $N_{J_i}^0$ is the concentration of CO molecules initially excited by the IR pump laser to J_i , and δN_{J_f} is the small concentration found in level J_f at the delay of δt .

For a given J_f , $(\delta N_{J_f}/N_{J_i}^0)$ was estimated by comparing the intensities of lines from J_f in the short delay spectrum ($I_{J_f,\delta t}$) and in a second spectrum recorded at 5 μs delay ($I_{J_f,e}$), taking into account any appropriate factors to correct for different CO flows and different settings on the gated integrator. Because rotational relaxation was complete and vibrational relaxation insignificant at $\delta t=5 \mu\text{s}$, the intensity which the selected line would have had if all the initially excited CO molecules had been transferred to the level J_f could be estimated by dividing $I_{J_f,e}$ by $f_{J_f,e}$, the fraction of the CO molecules occupying J_f at the longer delay. Consequently, $(\delta N_{J_f}/N_{J_i}^0)$ was given by $I_{J_f,\delta t}/(I_{J_f,e}/f_{J_f,e})I_{J_f,\delta t}/(I_{J_f,e}/f_{J_f,e})$. This method meant that no allowance had to be made for differences in line strength factors or laser intensities at different frequencies.

IV. RESULTS

A. The rate coefficients for total removal from selected rovibronic levels

Table I presents the second-order rate coefficients for the total removal of CO molecules from the rotational levels $J_i=0, 1, 4$, and 6 in the $(X^1\Sigma^+, v=2)$ vibronic state in collisions with He at 15, 27, 63, 149 and 294 K. Rate coefficients could not be obtained for removal from $J_i=0$ at 149 and 294 K because of a close overlap between the $R(0)$ and $R(10)$ lines in the VUV spectrum. At lower temperatures, insufficient population is created in $J=10$ for this to cause any problems.

Table I also lists the thermally averaged cross sections determined by dividing the rate coefficients by the mean relative velocities in CO-He collisions at the temperatures of the experiments. The uncertainties associated with quantities listed in Table I are quoted at the 2σ level, where σ is the standard error derived from the nonlinear least squares

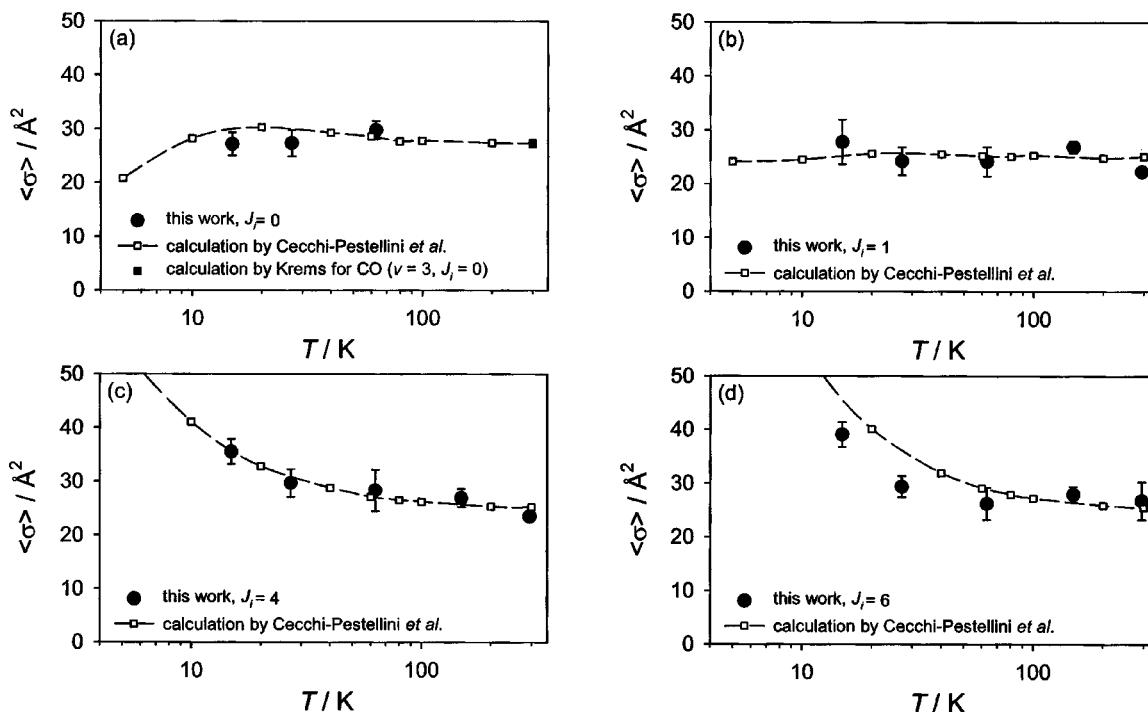


FIG. 3. Plots of thermally averaged cross section for the total removal of CO molecules from selected rotational levels J_i in collisions with He atoms at different temperatures: (a) for $J_i = 0$, (b) for $J_i = 1$, (c) for $J_i = 4$, and (d) for $J_i = 6$. The filled circles show the results of this work, while the open squares (joined by a dashed line) show the theoretical results of Cecchi-Pestellini *et al.* (Ref. 27) and the filled square in (a) shows the result of Krems (Ref. 28) for $\text{CO}(X^1\Sigma^+, \nu = 3, J_i = 0)$.

fittings of the individual decay traces, such as those shown in Fig. 2.

To illustrate the variation of the thermally averaged cross sections for transfer from different J_i levels with temperature, we show these quantities plotted against temperature in Fig. 3. Our experimental results are also compared in Fig. 3 with the theoretical results of Cecchi-Pestellini *et al.*,²⁷ which are given in the last row of Tables II–VI. As Cecchi-Pestellini *et al.* only published state-to-state rate coefficients for collisions involving negative ΔJ , we have used the principle of detailed balance to calculate the missing state-to-state rate coefficients. The sum of state-to-state rate coeffi-

cients from the level in question was then calculated, and converted to the thermally averaged cross section. While these theoretical results refer to CO in its ground vibrational state, and the experimental results were obtained for CO in its $\nu = 2$ vibrational state, it would appear that there is very little dependence of the rotational cross sections on vibrational state for CO. This is confirmed by Krems²⁸ who calculated total rate coefficients for rotational relaxation from $\text{CO } J = 0$ in a variety of vibrational states from $\nu = 1$ to 10. Krems' values for $\nu = 1$ and $\nu = 3$ differ by less than 0.3%, and the latter value is shown in Fig. 3 with the other results for $J = 0$.

TABLE II. Uncorrected and normalized (and corrected) state-to-state rate coefficients ($k_{J_i, J_f} / 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for transfer between selected initial (J_i) and specific final (J_f) rotational states in collisions between CO and He at 15 K.

	$J_i = 0$		$J_i = 1$		$J_i = 4$	
	Uncorrected	Normalized	Uncorrected	Normalized	Uncorrected	Normalized
$J_f = 0$	J_i	J_i	1.9 ± 0.3	3.5 ± 0.55	0.15 ± 0.1	0.4 ± 0.3
$J_f = 1$	8.8 ± 1.2	4.4 ± 0.6	J_i	J_i	0.44 ± 0.1	1.2 ± 0.3
$J_f = 2$	5.3 ± 0.9	2.7 ± 0.5	2.1 ± 0.5	3.9 ± 0.9	1.02 ± 0.2	2.7 ± 0.5
$J_f = 3$	1.2 ± 0.4	$1.02^{a} \pm 0.2$	0.45 ± 0.2	$0.94^{a} \pm 0.2$	2.4 ± 0.5	6.2 ± 1.5
$J_f = 4$					J_i	J_i
$J_f = 5$					0.07 ± 0.02	0.19 ± 0.05
$J_f = 6$						
Scaling factor		0.505		1.83		2.64
$\sum_f k_{J_i, J_f}$ (expt.)	15.3 ± 1.5		4.5 ± 0.6		4.0 ± 0.6	
$k_{J_i, \text{all } J_f}$	8.2 ± 0.6		8.3 ± 1.2		10.7 ± 0.7	
$\sum_f k_{J_i, J_f}$ (theor)	8.8		7.5		10.8	

^aThese numbers have been corrected by estimating $N_{J_f}^0$ from the Boltzmann plots having eliminated outliers according to the procedure described in the text. Having performed any corrections of this kind, the state-to-state rate coefficients are then normalized using the scaling factors given in the tables.

TABLE III. Uncorrected and normalized (and corrected) state-to-state rate coefficients ($k_{J_i, J_f}/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for transfer between selected initial (J_i) and specific final (J_f) rotational states in collisions between CO and He at 27 K.

	$J_i=0$		$J_i=1$		$J_i=4$	
	Uncorrected	Normalized	Uncorrected	Normalized	Uncorrected	Normalized
$J_f=0$	J_i	J_i	3.0 ± 0.5	2.6 ± 0.4	1.2 ± 0.8	0.4 ± 0.3
$J_f=1$	5.9 ± 0.9	5.3 ± 0.8	J_i	J_i	6.7 ± 1.4	2.4 ± 0.5
$J_f=2$	4.5 ± 1.2	4.1 ± 1.1	7.0 ± 0.8	$4.3^a \pm 0.5$	5.5 ± 1.0	2.0 ± 0.4
$J_f=3$	$1.8_5 \pm 0.7$	1.7 ± 0.6	$1.8_5 \pm 0.5$	1.6 ± 0.4	8.4 ± 1.2	$3.9^a \pm 0.4$
$J_f=4$			$0.9_5 \pm 0.5$	0.8 ± 0.4	J_i	J_i
$J_f=5$			0.43 ± 0.9	0.4 ± 0.8	7.8 ± 1.2	2.8 ± 0.4
$J_f=6$					1.7 ± 3.4	0.6 ± 1.2
Scaling factor		0.901		0.875		0.357
$\Sigma_f k_{J_i, J_f}$ (expt.)	12.3 ± 1.7		13.2 ± 1.6		31.2 ± 4.6	
$k_{J_i, \text{all } J_f}$	11.1 ± 1.0		9.8 ± 1.1		12.0 ± 1.0	
$\Sigma_f k_{J_i, J_f}$ (theor)	12.0		10.3		12.4	

These numbers have been corrected by estimating $N_{J_i}^0$ from the Boltzmann plots having eliminated outliers according to the procedure described in the text. Having performed any corrections of this kind, the state-to-state rate coefficients are then normalized using the scaling factors given in the tables.

B. Determination of rate coefficients for state-to-state rotational energy transfer

Tables II–VI present the values of state-to-state rate coefficients for transfer of CO molecules from levels ($X^1\Sigma^+$, $v=2$, $J_i=0, 1, 4$, and 6) in collisions with He at all five temperatures at which we have performed experiments. Under each value of J_i at each temperature, there are two columns of numbers. Those in the left-hand column are the rate coefficients that were determined according to the analysis set out in Sec. III B above. At the foot of each of these columns we give the sum of the individual state-to-state rate coefficients for transfer from a given initial rotational level J_i , i.e., $\Sigma_f k_{J_i, J_f}$. These sums are compared with the values of the rate coefficients for total removal determined in the kinetic experiments, i.e., $k_{J_i, \text{all } J_f}$, which are given in the row below the values of $\Sigma_f k_{J_i, J_f}$. Clearly, as collisions between CO and He only cause rotational energy transfer, these two quantities should be the same for each value of J_i at a

given temperature. The agreement between the values of $\Sigma_f k_{J_i, J_f}$ and $k_{J_i, \text{all } J_f}$ is quite good in most, but not all, cases. Considering the complete data set suggests the presence of a source of error in some of the experimental measurements. The excellent agreement between the values of $k_{J_i, \text{all } J_f}$ and $\Sigma_f k_{J_i, J_f}$ derived from the calculations of Cecchi-Pestellini *et al.*,²⁷ as well as other considerations, suggest that this source of error was more likely to be in the spectroscopic experiments rather than the kinetic measurements.

In our efforts to locate the source of such errors, we first checked the accuracy of our measurements at the longer (5 μ s) time delay, by preparing “Boltzmann plots” of the rotational level populations derived from these experiments. These equilibrium populations were measured via the Q -branch transitions in the $A^1\Pi-X^1\Sigma(0,2)$ band of CO for which the intensities ($I_{J,e}$) should be proportional to $(2J+1)\exp[-J(J+1)hcB_{v=2}/k_B T]$ where $B_{v=2}$ is the rotational

TABLE IV. Uncorrected and normalized (and corrected) state-to-state rate coefficients ($k_{J_i, J_f}/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for transfer between selected initial (J_i) and specific final (J_f) rotational states in collisions between CO and He at 63 K.

	$J_i=0$		$J_i=1$		$J_i=4$		$J_i=6$	
	Uncorrected	Normalized	Uncorrected	Normalized	Uncorrected	Normalized	Uncorrected	Normalized
$J_f=0$	J_i	J_i	2.3 ± 0.6	2.1 ± 0.5	2.6 ± 0.1	2.4 ± 0.1		
$J_f=1$	$7.3_5 \pm 1.4$	8.0 ± 1.5	J_i	J_i	$2.0_5 \pm 0.5$	1.9 ± 0.5		
$J_f=2$	5.4 ± 1.1	5.4 ± 1.2	6.8 ± 0.8	6.1 ± 0.7	2.7 ± 0.5	2.5 ± 0.5		
$J_f=3$	4.2 ± 1.0	4.6 ± 1.1	3.6 ± 0.7	3.2 ± 0.6	5.1 ± 0.5	4.7 ± 0.5	1.6 ± 0.4	2.3 ± 0.6
$J_f=4$			4.1 ± 0.9	3.7 ± 0.8	J_i	J_i	1.6 ± 0.5	2.3 ± 0.7
$J_f=5$					4.1 ± 0.6	3.8 ± 0.6	4.8 ± 1.0	7.0 ± 1.5
$J_f=6$					1.3 ± 0.4	$1.6^a \pm 0.4$	J_i	J_i
$J_f=7$					0.7 ± 0.3	0.7 ± 0.3	4.3 ± 2.4	$4.5^a \pm 2.4$
Scaling factor		1.08		0.899		0.919		1.47
$\Sigma_f k_{J_i, J_f}$ (expt.)	16.9 ± 2.0		16.8 ± 1.5		18.7 ± 1.1		12.3 ± 2.7	
$k_{J_i, \text{all } J_f}$	18.4 ± 1.1		15.7 ± 1.7		17.5 ± 2.4		16.2 ± 1.9	
$\Sigma_f k_{J_i, J_f}$ (theor)	17.7		15.7		16.7		17.9	

TABLE V. Uncorrected and normalized (and corrected) state-to-state rate coefficients ($k_{J_i, J_f}/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for transfer between selected initial (J_i) and specific final (J_f) rotational states in collisions between CO and He at 149 K.

Uncorrected	$J_i=0$		$J_i=1$		$J_i=4$		$J_i=6$	
	Normalized	Uncorrected	Normalized	Uncorrected	Normalized	Uncorrected	Normalized	
$J_f=0$	J_i	J_i						
$J_f=1$	17.5 ± 4.0	17.5 ± 4.0	J_i	J_i	$1.8_5 \pm 1.0$	1.3 ± 0.7	0.97 ± 0.2	1.9 ± 0.4
$J_f=2$	9.4 ± 1.6	9.4 ± 1.6	5.5 ± 0.4	$8.5^a \pm 0.6$	5.1 ± 1.1	3.6 ± 0.8	0.99 ± 0.2	1.9 ± 0.4
$J_f=3$	12.0 ± 2.0	12.0 ± 2.0	4.2 ± 0.4	4.2 ± 0.4	6.3 ± 1.3	4.4 ± 0.9	$2.2_5 \pm 0.2$	4.3 ± 0.4
$J_f=4$	3.1 ± 1.3	3.1 ± 1.3	4.7 ± 0.4	4.7 ± 0.4	J_i	J_i	1.5 ± 0.2	2.9 ± 0.4
$J_f=5$	4.1 ± 1.4	4.1 ± 1.4	0.93 ± 0.3	0.93 ± 0.3	12.1 ± 1.3	8.5 ± 0.9	$1.6_5 \pm 0.1$	3.2 ± 0.2
$J_f=6$			1.9 ± 0.5	1.9 ± 0.5	5.5 ± 0.8	3.9 ± 0.6	J_i	J_i
$J_f=7$			0.83 ± 0.4	0.83 ± 0.4	3.5 ± 0.8	2.4 ± 0.6	2.8 ± 0.2	5.4 ± 0.4
$J_f=8$					2.1 ± 0.7	1.5 ± 0.5	1.1 ± 0.1	$2.9^a \pm 0.2$
$J_f=9$							1.8 ± 0.2	3.5 ± 0.4
$J_f=10$							0.3 ± 0.1	0.5 ± 0.2
Scaling factor		No scaling		No scaling		0.700		1.92
$\Sigma_f k_{J_i, J_f}$ (expt.)	46.0 ± 5.1		18.1 ± 1.0		36.4 ± 2.7		13.4 ± 0.5	
$k_{J_i, \text{all } J_f}$	No data		25.5 ± 1.0		25.5 ± 1.6		26.5 ± 1.3	
$\Sigma_f k_{J_i, J_f}$ (theor)	25.9		23.5		24.1		24.9	

^aThese numbers have been corrected by estimating $N_{J_i}^0$ from the Boltzmann plots having eliminated outliers according to the procedure described in the text. Having performed any corrections of this kind, the state-to-state rate coefficients are then normalized using the scaling factors given in the tables.

constant for CO in the ($X^1\Sigma^+, v=2$) state. In Fig. 4, we present two such plots. In panel (b) for $J_i=0$ and $T=27$ K, where $\Sigma_f k_{J_i, J_f}$ and $k_{J_i, \text{all } J_f}$ agree to within 11%, all the points fall on or close to the line describing the equilibrated Boltzmann distribution. By contrast, in panel (a) for $J_i=0$ and $T=294$ K, three points fall significantly off the line. Unfortunately, owing to spectroscopic interference with higher rotational levels, there is no value of the rate coefficient for total removal from this level at this temperature.

Given these differences, we have adopted a procedure based on Chauvenet's criterion²⁹ to determine the quality of the raw Boltzmann plots and, more specifically to determine

whether any of the individual intensities in the long delay spectrum were "outliers," as a result of some recording error. The first step in the iterative procedure was to fit the whole of the measured data set to the Boltzmann equation. The second step was to remove each individual point in turn and calculate the average deviation without that point. If the omitted point was then more than two average deviations from the fit, the point was designated as an outlier and was eliminated from the plot. The remainder of the data was then refitted to the Boltzmann equation and the average deviation recalculated. The procedure was repeated to identify further outliers using the 2σ criterion. It was decided to set a maxi-

TABLE VI. Uncorrected and corrected state-to-state rate coefficients ($k_{J_i, J_f}/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for transfer between selected initial (J_i) and specific final (J_f) rotational states in collisions between CO and He at 294 K.

	$J_i=0$		$J_i=1$		$J_i=4$		$J_i=6$	
	Uncorrected	Normalized	Uncorrected	Normalized	Uncorrected	Normalized	Uncorrected	Normalized
$J_f=0$	J_i	J_i						
$J_f=1$	7.7 ± 1.1	7.7 ± 1.1	J_i	J_i	2.4 ± 0.3	1.8 ± 0.2	0.68 ± 0.2	0.95 ± 0.3
$J_f=2$	4.7 ± 0.3	$7.1^a \pm 0.5$	6.6 ± 0.4	$10.4^a \pm 0.7$	2.1 ± 0.1	$3.2^a \pm 0.1$	0.44 ± 0.1	$1.1^a \pm 0.2$
$J_f=3$	6.0 ± 0.4	6.0 ± 0.4	3.4 ± 0.3	3.4 ± 0.3	10.0 ± 0.8	8.3 ± 0.7	1.9 ± 0.2	2.7 ± 0.3
$J_f=4$	$1.6_5 \pm 0.4$	$1.6_5 \pm 0.4$	4.4 ± 0.3	4.4 ± 0.3	J_f	J_i	2.9 ± 0.2	4.1 ± 0.4
$J_f=5$	3.4 ± 0.3	3.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	6.8 ± 0.3	5.2 ± 0.2	5.1 ± 0.2	27.0 ± 0.3
$J_f=6$	1.1 ± 0.2	$1.6^a \pm 0.3$	2.7 ± 0.3	2.7 ± 0.3	2.9 ± 0.1	$3.8^a \pm 0.1$	J_i	J_i
$J_f=7$	2.7 ± 0.3	2.7 ± 0.3	1.3 ± 0.3	1.3 ± 0.3	4.8 ± 0.2	3.6 ± 0.2	6.0 ± 0.2	8.4 ± 0.3
$J_f=8$	0.92 ± 0.3	0.92 ± 0.3	1.5 ± 0.3	1.5 ± 0.3	2.3 ± 0.2	1.8 ± 0.2	2.8 ± 0.2	4.0 ± 0.3
$J_f=9$	1.1 ± 0.3	1.1 ± 0.3	0.77 ± 0.3	0.77 ± 0.3	2.8 ± 0.3	2.1 ± 0.3	2.8 ± 0.2	4.0 ± 0.3
$J_f=10$			0.67 ± 0.3	0.67 ± 0.3	0.62 ± 0.1	0.47 ± 0.1	0.93 ± 0.1	$1.9_5^a \pm 0.2$
$J_f=11$					0.74 ± 0.2	0.56 ± 0.2	1.0 ± 0.2	1.4 ± 0.3
$J_f=12$					0.26 ± 0.2	0.19 ± 0.2		
Scaling factor		No scaling		No scaling		0.767		1.40
$\Sigma_f k_{J_i, J_f}$ (expt.)	29.4 ± 1.4		22.7 ± 0.9		36.6 ± 1.1		24.6 ± 0.5	
$k_{J_i, \text{all } J_f}$	no data		29.7 ± 0.7		31.3 ± 0.9		35.7 ± 4.7	
$\Sigma_f k_{J_i, J_f}$ (theor)	36.7		33.6		33.8		34.1	

^aThese numbers have been corrected by estimating $N_{J_i}^0$ from the Boltzmann plots having eliminated outliers according to the procedure described in the text. Having performed any corrections of this kind, the state-to-state rate coefficients are then normalized using the scaling factors given in the tables.

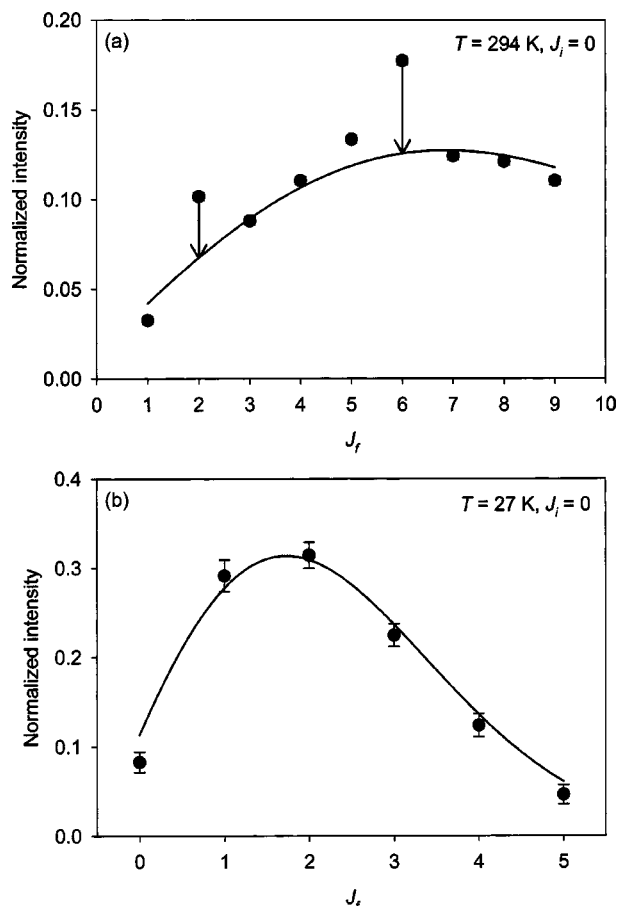


FIG. 4. Boltzmann plots testing the quality of the DR spectra recorded at a delay of 5 μ s. In each case, the measured LIF intensities of the Q -branch transitions ($A^1\Pi, v=0, J-X^1\Sigma^+, v=2, J$) are plotted against J_f . The solid line corresponds to a fit of the final data set (with outliers excluded as described in the text) to a function of the form $Z(2J_f+1) \times \exp[-hcB_{v=2}J_f(J_f+1)/k_B T]$ where Z was allowed to float. Panel (a) shows results for $J_i=0$ and $T=294$ K, with two outliers identified and panel (b) shows results for $J_i=0$ and $T=27$ K, with no outliers identified.

num of two outliers for each set of data. According to these criteria, 13 of the Boltzmann plots were satisfactory, three had one outlier and two had two outliers. Further, some of the outliers were from measurements on the level J_i , and were not therefore used in any calculation of $\delta N_{J_f}/N_{J_i}^0$. Out of the complete set of data only 15 out of 109 calculations of state-to-state rate coefficients were affected by this correction in the value of $\delta N_{J_f}/N_{J_i}^0$. In these cases, the intensity $I_{\text{LIF},J}$ at the longer delay was recalculated by interpolation on the Boltzmann plot and the corresponding state-to-state rate coefficient was recalculated.

With so few data requiring correction because of a poor measurement of $I_{\text{LIF},J}$ at 5 μ s, it seems that other sources of error must have been significant. Of course, it was impossible to test for errors in the spectral intensities measured at δt . Another possibility is that experimental errors might occur in the value of δt .

For this reason, we decided to recalculate the state-to-state rate coefficients, including any values corrected because of perceived error in the measurement of $I_{\text{LIF},J}$ at 5 μ s, by “normalizing” them; that is, by multiplying each value by

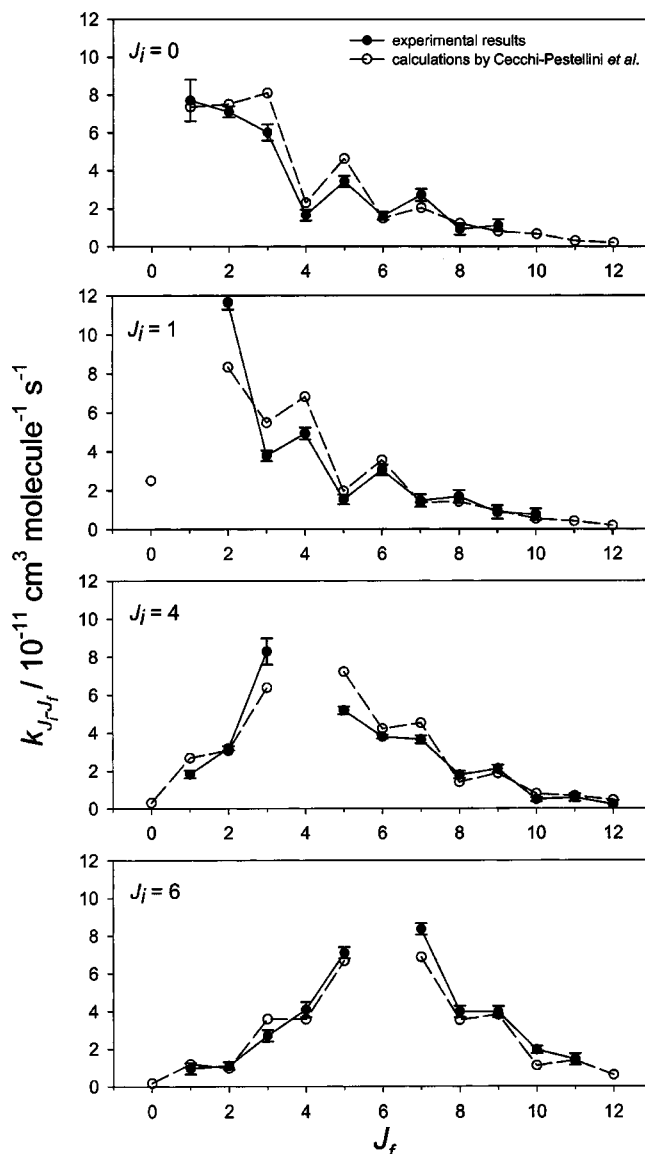


FIG. 5. Corrected and normalized state-to-state rate coefficients for rotationally inelastic collision between $\text{CO}(X^1\Sigma^+, v=2, J_i=0, 1, 4, \text{ and } 6)$ and He at 294 K. The filled circles (joined by a solid line) show the data obtained in the experiments reported in this paper, the open circles (joined by a dashed line) show the theoretical results of Cecchi-Pestellini *et al.* (Ref. 27).

$(\sum_f k_{J_i, J_f} / k_{J_i, \text{all } J_f})$. The numbers listed in the right hand of the two columns under each value of J_i in Tables II–VI are those corrected and renormalized state-to-state rate coefficients. Those referring to the footnote are the rate coefficients that have been corrected, before the normalization, by using values of $I_{\text{LIF},J}$ at 5 μ s obtained by interpolation on the Boltzmann plots. There are a few cases where normalization could not be justified or carried out. For example, in the instances of $J_i=0, T=149$ K and $J_i=0, T=294$ K, it was not possible to measure values of $k_{J_i, \text{all } J_f}$ because of the overlap between the $R(0)$ and $R(10)$ lines in the $A^1\Pi-X^1\Sigma(0,2)$ band. The same overlap also prevented us from obtaining the state-to-state rate coefficients $k_{1,0}$ which are expected to be large and to contribute significantly to the sum $\sum_f k_{J_i, J_f}$.

Figures 5–7 display the corrected and normalized state-to-state rate coefficients graphically for sets of data at three

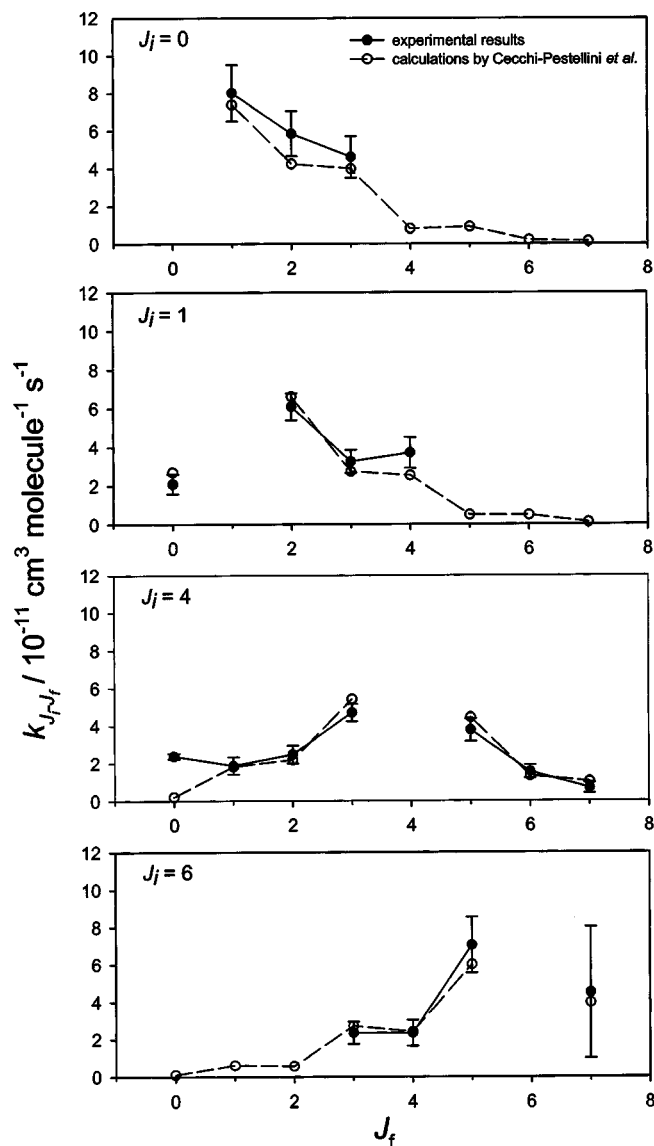


FIG. 6. Corrected and normalized state-to-state rate coefficients for rotationally inelastic collision between CO ($X^1\Sigma^+$, $v=2$, $J_i=0, 1, 4$, and 6) and He at 63 K. The filled circles (joined by a solid line) show the data obtained in the experiments reported in this paper, the open circles (joined by a dashed line) show the theoretical results of Cecchi-Pestellini *et al.* (Ref. 27).

temperatures: 294, 63, and 15 K. These experimental data are compared with the results of the close-coupling calculations performed by Cecchi-Pestellini *et al.*²⁷ We emphasize that no normalization of any kind has been undertaken between the experimental and theoretical results. The agreement between the two sets of data is excellent.

V. DISCUSSION

The thermally averaged cross sections for total removal from selected rotational levels show only a minor dependence on temperature. What variation there is reflects the effect of two factors. At lower temperatures, the weak intermolecular attraction between CO and He slightly increases the cross section for “core collisions.” This factor is probably responsible for the increase in the thermal cross-sections for $J_i=4$ and 6 shown in panels (c) and (d) of Fig. 3. For

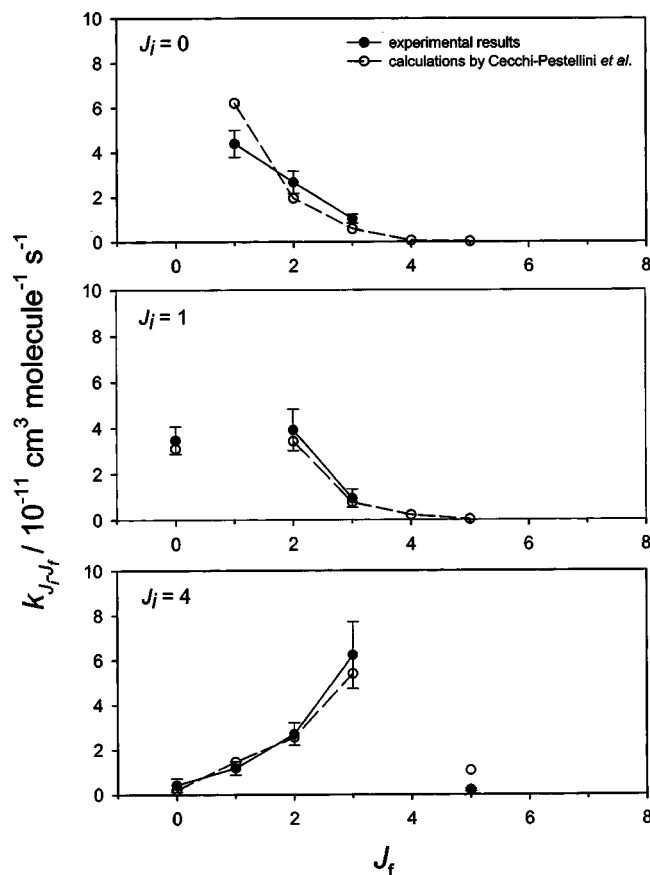


FIG. 7. Corrected and normalized state-to-state rate coefficients for rotationally inelastic collision between CO ($X^1\Sigma^+$, $v=2$, $J_i=0, 1$, and 4) and He at 15 K. The filled circles (joined by a solid line) show the data obtained in the experiments reported in this paper, the open circles (joined by a dashed line) show the theoretical results of Cecchi-Pestellini *et al.* (Ref. 27).

lower J_i , especially for $J_i=0$, this effect will be opposed by the paucity of transitions with $J_i > J_f$, and the fact that the transitions with $J_f > J_i$ have an endothermicity that is significant relative to $k_B T$, thereby reducing the rate coefficients for such processes. This effect leads to the decrease in the cross section observed in the theoretical data for $J_i=0$, which explores temperatures as low as 5 K and may explain why the experimental data for $J_i=0$ and 1 show no significant dependence down to 15 K, in contrast to the results for $J_i=4$ and 6 .

The state-to-state rate coefficients, both those shown in Figs. 5–7 and those for $T=27$ K and $T=149$ K which are not displayed graphically, exhibit a number of general features: First, for all J_i and temperatures, the rate coefficients $k_{J_i \rightarrow J_f}$ show a general decrease with increasing ΔJ . Second, superimposed on this general trend, the rate coefficients oscillate with ΔJ , showing a propensity to favor odd ΔJ over even ΔJ , as found by Antonova *et al.*¹⁵ This behavior is most marked in the data for higher temperatures and is most clearly apparent in the data for 294 K shown in Fig. 5. Third, the distribution of the rate coefficients $k_{J_i \rightarrow J_f}$ with ΔJ narrows as the temperature is reduced. Finally, transitions with $J_f < J_i$ are favored with respect to transitions with $J_f > J_i$ more strongly as the temperature is lowered and, at all temperatures, as J_i is increased.

Apart from the oscillatory behavior, the other propensities are commonly found in rotationally inelastic collisions between simple molecules and atoms. In particular, they echo behavior that was found in earlier low temperature experiments on energy transfer in collisions between $\text{NO}(X^2\Pi_{3/2}, v=3)$ and He, Ar, and N_2 . The results of such collisions are also found to exhibit oscillatory behavior. However, in the case of $\text{NO}(X^2\Pi_{3/2}, v=3) + \text{He}$, for example, the oscillations are in the opposite sense; that is, even ΔJ are favored over odd ΔJ . Our finding for CO-He is consistent with that found by Antonova *et al.*¹⁵ in their crossed molecular beam study but opposite to that found by Phipps *et al.*¹ in their IR-IR DR study of CO-CO collisions.

The preference for odd over even ΔJ transitions has been explained by McCurdy and Miller.¹⁷ They used classical *S*-matrix theory to examine the cross sections for rotationally inelastic collisions between a diatomic molecule and an atom with a closed electronic shell, as they systematically varied the relative amounts of even and odd anisotropies in a representative potential energy surface. As the odd anisotropy of the potential is increased, the cross sections for odd ΔJ transitions increase until they are larger than those for even ΔJ . The observation that odd ΔJ transitions are favored in rotationally inelastic CO-He collisions demonstrates that the CO-He interaction potential must be particularly anisotropic.

In addition to our experimental data, Figs. 5–7 show the theoretical state-to-state rate coefficients calculated by Cecchi-Pestellini *et al.*²⁷ using the SAPT potential of Heijmen *et al.*¹⁸ The agreement between experiment and theory for these data (and for those at 63 and 149 K, which are not shown) is excellent. In addition, we recall that the agreement between the theoretical and experimental values of the rate coefficients for total removal from selected rotational levels (see Fig. 3) is also excellent. We note that the rate coefficients calculated by Cecchi-Pestellini *et al.* agree to within about 30% with those from earlier calculations³⁰ on CO-He collisions, and are comparable to those calculated³¹ for collisions between CO and *ortho*- and *para*- H_2 .

VI. SUMMARY AND CONCLUSIONS

We have reported the most extensive set of rate coefficients for rotationally inelastic collisions between CO molecules in their electronic ground state and helium atoms that has yet been compiled. This data set includes rate coefficients for total removal from selected rotational levels J_i in the $X^2\Pi$, $v=2$ vibronic state, as well as rate coefficients for transfer between selected initial (J_i) and specific final (J_f) rotational states. Results have been obtained at five temperatures: 294, 149, 63, 27, and 15 K. Our experimental results have been compared with the latest, extensive, theoretical calculations of Cecchi-Pestellini *et al.*²⁷ The agreement is remarkable and, *inter alia*, confirms the accuracy of the CO-He potential energy surface calculated by Heijmen *et al.*¹⁸ and used in the calculations of Cecchi-Pestellini *et al.*, at least the parts of this surface explored by CO-He thermal collisions in the temperature range reported here, $T=15\text{--}295$ K.

These studies provide the astrophysical community with reliable data on which to base their models involving CO-He

collisions. Of course, the most abundant species in dense interstellar clouds is H_2 , not He. It is planned to extend the measurements that we have described in the present paper to the study of rotationally inelastic collisions between CO and H_2 . Together with the results in the present paper these measurements should provide modelers with the information required to interpret measurements on the intensities of rotational transitions on CO observed from the interstellar medium.

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